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Observation of photocurrent generation in electrodeposited zinc oxide layers

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Abstract

Wurtzite zinc oxide (ZnO) films with band gap energy of about 3.3 eV were deposited onto conductive substrates by electrodeposition from a simple aqueous zinc nitrate solution at 335 K. The films showed optical transmission around 70% in the visible light region. The electrical resistance showed a strong dependence on cathodic potential. The decrease in electrical resistance could be observed with light irradiation irrespective of the cathodic potential and was attributed to the excitation of electrons from valence band to conduction band by light with wavelength below 375 nm. A photocurrent of about 0.10 μA was generated for a cell composed of Ag electrode/Au/ZnO/NESA glass substrate under conditions of irradiation by sunlight.

1. Introduction

Zinc oxide (ZnO) is of considerable interest in the optical and electronic industries, because of its electrical, optical and acoustic properties. ZnO films are prepared by several techniques, such as radio frequency magnetron sputtering, chemical vapour deposition and molecular beam epitaxy. Preparation of oxide films by electrodeposition from aqueous solution presents several advantages over other techniques: (i) the thickness and morphology can be controlled using electrochemical parameters, (ii) relatively uniform films can be obtained on substrates of complex shape, (iii) the deposition rate is relatively high, (iv) the equipment is not expensive, and (v) films can be prepared on substrates with melting point below 100 °C [1].

It has been reported that a wurtzite ZnO film with high optical transparency can be prepared by cathodic deposition from a simple zinc nitrate aqueous solution [1–3]. Since the ZnO film showed direct band gap energy of 3.3 eV [4], it is expected that some photocurrent can be generated with irradiation of light with wavelength below 375 nm.

In this work semiconducting ZnO films is prepared by cathodic deposition at various cathodic potentials from an aqueous solution and their electrical characteristics and dependence on light irradiation are investigated.

2. Experimental details

2.1. *Film preparation*

ZnO films of 1 μm in thickness were prepared by cathodic deposition from a 0.1 M zinc nitrate aqueous solution at 335 K. The solution was prepared with distilled water and reagent-grade chemicals. A soda-lime glass coated with conductive tin oxide (NESA glass, approximately 10 Ω, Nippon Sheet Glass Co., Ltd) was used as the cathode. Prior to electrodeposition, the NESA glass cathodes (50 mm × 50 mm × 1.0 mm) were rinsed in acetone, anodically polarized in 1 M NaOH aqueous solution and then rinsed with distilled water. Zinc sheet (99.999% purity) was used as active anode and an Ag/AgCl electrode as reference. Electrodeposition was carried out potentiostatically between −0.7 and −1.0 V using a potentiostat–galvanostat without stirring.

2.2. *Structural characterization*

X-ray diffraction measurements were performed using monochromated CuK_α radiation at 40 kV and 50 mA (MAC Science, MXP18). The diffraction angles were referenced to those from a high-purity silicon powder.

2.3. *Optical characterization*

Optical characterizations were performed on films by using a dual-beam spectrophotometer (Shimazu UV-2200) by scanning the wavelength from 200 to 700 nm

with reference to air. Optical bandgap energies were calculated from the absorption edge in absorption spectra with reference to the substrate glass.

2.4. *Electrical characterization*

Figure 1 shows a schematic view of samples used for electrical resistance measurements. Comb-shaped electrodes [5] with spacing of 1 mm were formed on the ZnO films by a screen-printing technique with a silver paste (DS-2220 Okuno Chemical Co., Ltd) and by drying in air at ambient temperature. Electrical resistance between the comb-shaped electrodes was measured in dark or under light irradiation condition (5 mW cm^{-2}).

Figure 2 shows a configuration of a Ag electrode/Au/1 μm thick ZnO/NESA glass cell used for the evaluation of photocurrent generation. A 50 nm thick Au layer was deposited on the ZnO film by a sputtering technique. Ag electrodes were formed on the Au layer by the screen-printing technique with silver paste. Light irradiation was carried out in the direction normal to the sample surface at AM 1.5 illumination (100 mW cm^{-2}; 25 °C) for 1 min. A current between the conductive SnO_2 layer in the NESA glass and the screen-printed Ag electrode was measured with a multimeter.

3. Results and discussion

3.1. *Structural characterization*

Figure 3 shows X-ray diffraction patterns of ZnO films prepared at cathodic potentials from −0.7 to −1.0 V. All the diffraction lines seen in Figure 3 were identified as those from SnO_2 (NESA glass substrate) and ZnO with a wurtzite structure [6]. The preferred orientation showed a dependence on cathodic potential and a (0 0 0 1) oriented ZnO film was obtained at −0.7 V.

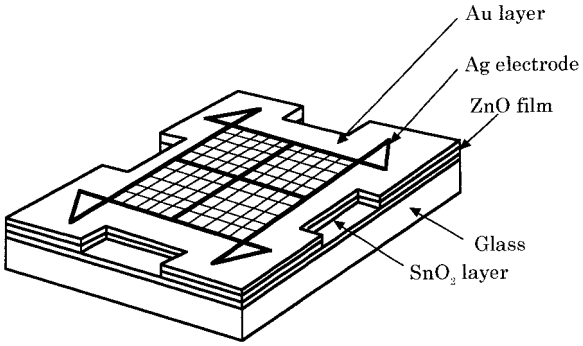

Fig. 2. Schematic view of Ag electrode/Au/ZnO/NESA glass cell.

3.2. *Optical characterization*

Figure 4 shows the optical transmission spectrum for 1 μm thick ZnO film prepared at −0.7 V. The optical transmission spectra were almost the same in profile for ZnO films prepared in the range from −0.7 to −1.4 V. The optical transmission decreased with decrease in wavelength and was approximately 70% at wavelength 600 nm. It was previously reported that the optical transparency strongly depended on the surface irregularity [2]. The high optical transmission suggested that the ZnO films had a smooth surface.

The optical absorption edge could be observed at a wavelength of about 375 nm, which corresponded to a bandgap energy of about 3.3 eV with the assumption of direct transition, regardless of cathodic potential. This bandgap energy is consistent with that for a nondoped ZnO film prepared by other techniques [7].

3.3. *Electrical characterization*

Figure 5 shows the resistances of ZnO films evaluated in the dark as a function of cathodic potential. Closed circles represent an average value for five measurements. A low resistance of 4 Ω was recorded for the 1 μm thick ZnO film prepared at −0.7 V, and the resistance

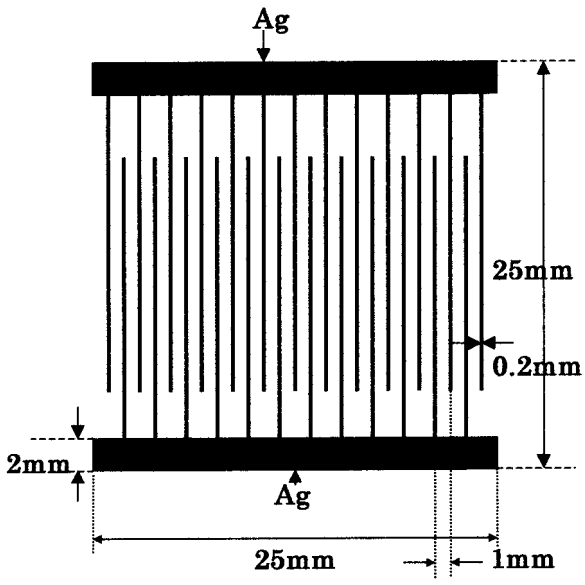

Fig. 1. Schematic configuration of a comb-shaped electrode used for measurement of resistance.

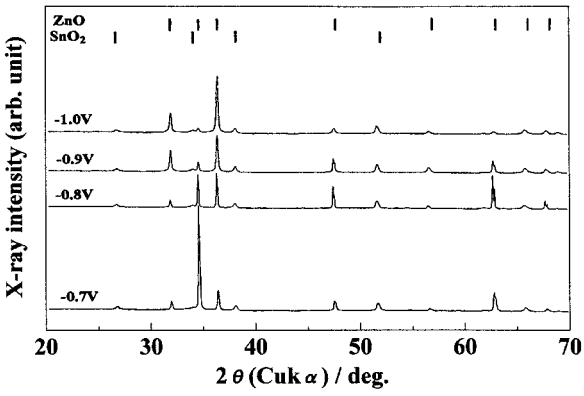

Fig. 3. X-ray diffraction spectra for ZnO films prepared at −0.7 to −1.0 V.

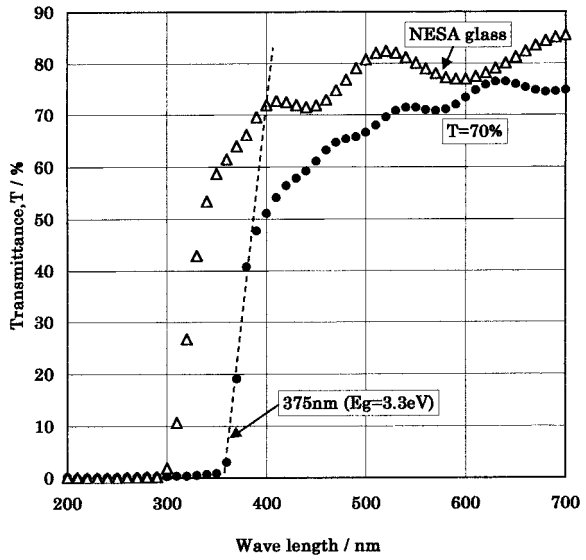

Fig. 4. Optical transmission spectra for NESA and ZnO film prepared at −0.7 V.

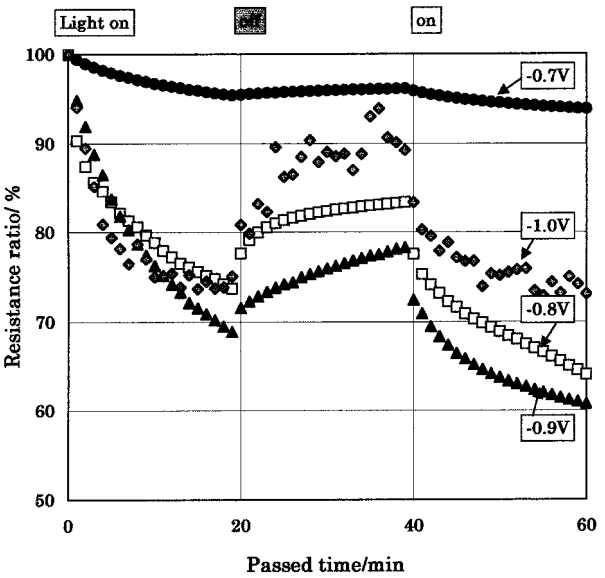

Fig. 6. Effects of light irradiation on resistance ratio for ZnO films prepared at −0.7 to −1.0 V.

increased to 160 Ω at the cathodic potential of −1.0 V. The resistances comprise both the ZnO film and the SnO_2 layer in NESA glass. The film thicknesses of these layers were maintained constant throughout the measurements. Therefore, the change in resistance with cathodic potential corresponds to differences in resistivity of the ZnO films.

Figure 6 shows the effects of light irradiation on the resistance ratio (R_{ratio}) for ZnO films. This was calculated using

$$R_{ratio} = \frac{R_{light}}{R_{dark}} \times 100 \quad (1)$$

where R_{light} and R_{dark} are the resistances measured under light irradiation and in dark, respectively. The abscissa represents time. The resistance ratio decreased with time, regardless of cathodic potential. No change in resistance ratio was observed for bare NESA glass substrate. The decreases in resistance ratio were attributed to ZnO films. The degree of decrease in resistance ratio depended on the cathodic potential and a maximum change of about 30% was observed for −0.9 V. The changes in resistance during 20 min irradiation were about 0.18, 20.3, 52.2 and 54.8 Ω for cathodic potentials of −0.7, −0.8, −0.9 and −1.0 V, respectively. The changes in electrical resistance corresponded to the resistivities of ZnO films as already mentioned. Since the ZnO films had an optical bandgap energy of 3.3 eV, the light of wavelength below 375 nm induced excitation of electrons from valence band to conduction band. The decreases in resistivity indicated that the excited electrons acted as a carrier in the ZnO films. The amount of increased carrier concentration, which was calculated from the mobility and carrier concentration in dark already reported [8], was almost constant and of order 10^{18} cm^{-3} for ZnO films prepared in the range from −0.7 to −0.9 V. The difference among the resistance ratios seen in Figure 6 can be attributed to an inverse relationship between resistivity (ρ) and carrier concentration (η); $\rho \propto 1/\eta$. The resistance ratio increased by stopping the light irradiation at 'off'. The recombination of electrons and holes, which were generated by light irradiation, took place in the dark and resulted in an increase in resistance ratio. For all ZnO films kept in dark for 20 min, the resistance ratios did not return to 100%; this was attributed to the imperfect recombination of electrons and holes. A holding time of about 100 min was needed to return the resistance ratio to 100%.

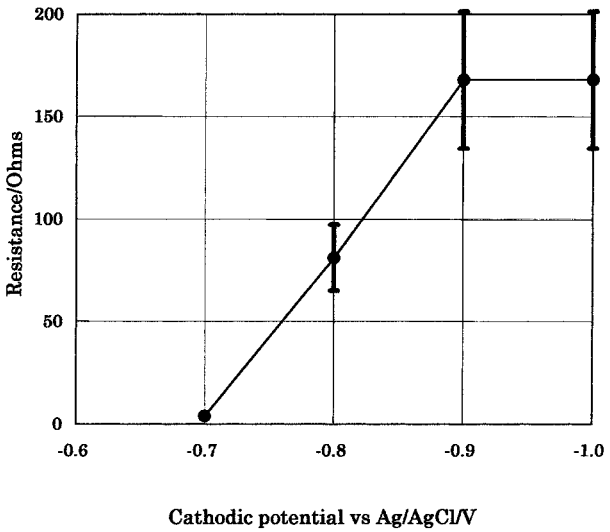

Fig. 5. Relationship between cathodic potential and resistance for ZnO films in dark.

Figure 7 shows the effect of irradiation by sunlight on the cell current for the system Ag electrode/Au/ZnO/NESA glass cell. These irradiations were carried out for 1 min. The ZnO film was prepared at −0.9 V, which

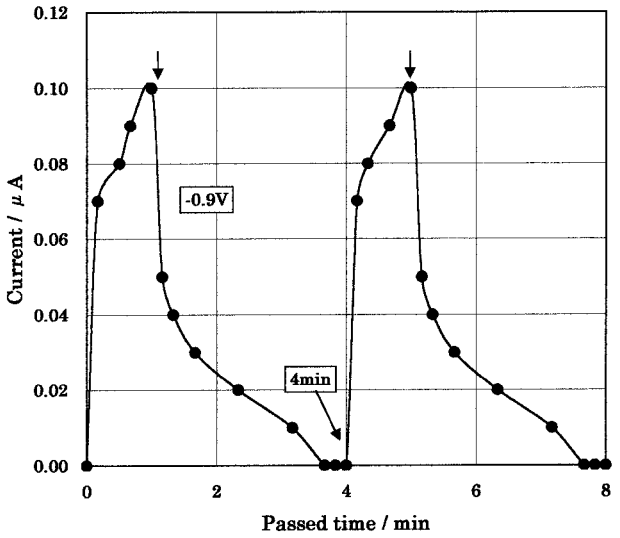

Fig. 7. Effect of light irradiation on current generation for Ag electrode/Au layer/ZnO/NESA glass cell.

gave the maximum change in resistance ratio in Figure 6. No change in current was observed for a Ag electrode/Au/NESA substrate in the absence of ZnO layer. The current increased with irradiation time and a maximum current of about 0.10 μA was obtained with 1 min irradiation. After light irradiation was stopped (represented by arrows in Figure 7), the current decreased to 0 μA with the passage of time in dark.

4. Conclusion

Wurtzite ZnO films with an optical bandgap energy of 3.3 eV were cathodically deposited on conductive glass substrates from a simple zinc nitrate aqueous solution at 335 K. The resistance showed a strong dependence on cathodic potential. A decrease in resistance was observed with light irradiation irrespective of the cathodic potential and was attributed to the excitation of electrons from the valence band to the conduction band by light irradiation below 375 nm wavelength. A photocurrent of 0.10 μA was generated in a Ag electrode/Au/ZnO/NESA glass cell under sunlight irradiation.

References

1. M. Izaki and T. Omi, *J. Electrochem. Soc.* **144** (1997) 1949.
2. M. Izaki and T. Omi, *Appl. Phys. Lett.* **68** (1996) 2439.
3. M. Izaki and T. Omi, *J. Electrochem. Soc.* **143** (1996) L53.
4. C. Kittel, 'Introduction to Solid State Physics', 6th edn (J. Wiley & Sons, New York, 1986), p. 183.
5. K. Tsuda, *Ceramics Japan* **25** (1990) 740 (in Japanese).
6. Joint Committee on Powder Diffraction Standards, Set 36, No. 1451, International Center for Diffraction Data, Swarthmore, PA (1990).
7. A.P. Roth, J.B. Webb and D.F. Williams, *Solid State. Commm.* **39** (1981) 1269.
8. M. Izaki and H. Enomoto, *Kagaku to Kogyo* **71** (1997) 111 (in Japanese).